

Stratospheric and Mesospheric HO_x: Results from Aura MLS and FIRS-2

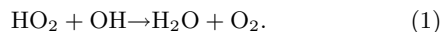
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Observations of OH and HO₂ from Aura MLS for four seasons and diurnal profiles from the FIRS-2 balloon instrument for Fall 2004 are compared with photochemical model simulations testing three sets of kinetics parameters. MLS and FIRS-2 OH profiles, between 25-60 km, are lower than model results using standard kinetics. Use of a faster, previously published rate constant for O+OH leads to better agreement with MLS and FIRS-2 profiles of OH. A 20% increase in the rate of HO₂+OH and the faster rate for O+OH results in improved overall agreement with observations of OH, HO₂, HO_x, and HO₂/OH. Since the MLS and FIRS observations of HO_x are reasonably well described by these models, they are therefore not consistent with the previously reported HO_x dilemma. However, all models considered here result in calculated odd oxygen loss exceeding production, consistent with the long standing ozone deficit problem.

1. Introduction

Simultaneous observations of OH and HO₂ from the Microwave Limb Sounder (MLS) instrument on board the Aura satellite, launched July 15, 2004, provide a unique opportunity to test our understanding of stratospheric HO_x (OH+HO₂). We present an analysis of daytime zonally averaged profiles of OH and HO₂ for four seasons using a photochemical model constrained by MLS observations of HO_x precursors. Measurements of OH and HO₂ acquired by the Far-Infrared Spectrometer (FIRS-2) instrument during an Aura validation balloon campaign in September 2004 are also examined.

In the stratosphere, OH is primarily produced through the reaction of water with metastable oxygen, O(¹D), and by water photolysis above 60 km. HO_x is lost primarily through the reaction

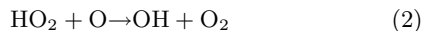


Previous observations of either OH or HO₂ alone have shown poor agreement with model simulations. As a result, two studies have suggested modifications to the rate constants of HO_x partitioning reactions to reach better agreement between measurements and model calculations (see auxiliary material for further discussion¹). Ground based microwave observations of HO₂ were used to sug-

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gest a 60-80% decrease in the rate of



[Clancy *et al.*, 1994]. Mesospheric OH observations by the Middle Atmospheric High Resolution Spectrograph Investigation (MAHRSI) instrument in November 1994 led to the suggestion of either a 50% reduction in the rate of reaction (2) or both a 20% reduction of rate (2) and a 30% increase in rate (1) [Summers *et al.*, 1997]. However, without simultaneous observations of OH and HO₂, it is difficult to attribute the above discrepancies to HO_x loss, production, or partitioning.

These suggested changes were tested against an OH profile measured by MAHRSI in August 1997 [Conway *et al.*, 2000]. Their results showed that the kinetic changes needed to match the MAHRSI OH profile above 50 km led to poorer agreement between modeled and measured OH from 35-45 km. No particular kinetics change allows models to reproduce MAHRSI OH in both the mesosphere and the upper stratosphere. This is known as the “HO_x dilemma” [Conway *et al.*, 2000].

Loss of odd-oxygen (O_x=O₃+O) is dominated by HO_x catalytic processes above 45 km. Ozone, the main component of O_x at these altitudes, should be in photochemical steady state. However, calculated loss of O_x generally exceeds production by ~35% [e.g. Jucks *et al.*, 1996, Osterman *et al.*, 1997]. This leads to an underprediction of upper stratospheric O₃, commonly known as the “ozone deficit problem”.

The kinetics changes suggested by Clancy *et al.* [1994] and Summers *et al.* [1997] lead to good agreement with measured mesospheric HO₂ and OH, respectively, and also largely resolve the ozone deficit problem. These results are driven by a reduction in the rate of (2), resulting in more HO₂, less OH, and slower O_x removal compared to a standard model. In contrast, Jucks *et al.* [1998] suggested the rates of reactions (1) and (2) must both be reduced by 25% to best explain FIRS-2 observations of OH and HO₂. The Jucks *et al.* [1998] kinetics change has a negligible effect on the ozone deficit problem. Below, we investigate the implications of recent Aura MLS and FIRS-2 observations for the HO_x dilemma and ozone deficit problem.

2. Measurements and Model

The Aura MLS instrument measures OH at 2.5 THz and HO₂ at 643 GHz [Pickett, 2006]. Validation of MLS OH and HO₂ by comparison with balloon-borne remote sensing measurements of these species is described by Pickett *et al.* [2006].

The MLS profiles presented here are 15 day zonal averages, spanning 34±10°N, centered on September 23 (fall) and December 23, 2004 (winter) as well as March 15 (spring) and June 15, 2005 (summer), based on version 1.51 of the retrieval software. The local solar time (LST) of the observations is ~13.30 hr. MLS observations of OH, HO₂, HO_x, and HO₂/OH are shown in Figure 1. Here, we only consider data below 60 km, because above 60 km only observations of OH are available [Pickett *et al.*, 2006]. Precision in the 15 day averages for OH and HO₂ is good with negligible uncertainty. The error bars in Figures 1a and 1b are equal to 10%, which represents our estimate of the uncertainty in instrument calibration (i.e., measurement accuracy) [Pickett *et al.*, 2006]. The MLS profiles of HO₂ (Figure 1b) exhibit oscillatory be-

havior that is likely a retrieval artifact [Pickett *et al.*, 2006]. This behavior will result in non-zero reduced chi square (χ^2_r) values even for a model that simulates quite well the overall shape and magnitude of HO_x species.

Observations from FIRS-2 were taken by a thermal emission far-infrared Fourier transform spectrometer [Jucks *et al.*, 1998] on board a balloon gondola launched from Ft. Sumner, NM (34.5°N, 104°W) on September 23, 2004. These profiles are from ~1 hour limb scans. Seven profiles, taken over the course of the day (7:30-17:00 LST), are used for statistical comparison. We consider all data below the balloon float altitude (38 km) and three points above (42, 44 and 48 km) to account for the poorer vertical resolution above float. The OH and HO₂ error bars are the root sum squared (RSS) combination of 1 σ estimates of accuracy and precision. Error bars for both HO_x and HO₂/OH shown in Figures 1c and 1d are the RSS propagation of the errors in OH and HO₂ from the respective instruments.

The photochemical model is constrained by MLS measurements of H₂O, O₃, N₂O, CO, and temperature for each season. The model assumes a balance of production and loss for each species integrated over 24 hrs and has been used in previous studies to analyze observations from balloon, satellite, and aircraft platforms [e.g., Pickett *et al.*, 2006, Jucks *et al.*, 1998]. Profiles of Cl_y, NO_y, and CH₄ are specified using well established tracer-tracer relations [Jucks *et al.*, 1998]. The model includes mesospheric chemistry and solar cycle effects, a new feature described in the auxiliary material of Pickett *et al.* [2006].

We show model results for several sets of kinetic parameters: a) JPL02 kinetics [Sander *et al.*, 2003] (hereafter Mdl_{JPL02}); b) same as JPL02 except the Smith and Stewart [1994] (hereafter SmSt94) rate constant for O+OH (Mdl_{SmSt}) c) same as Mdl_{SmSt}, except a 20% increase in the rate of HO₂+OH (Mdl_C). The SmSt94 rate constant for O+OH is ~20% faster than the JPL02 rate and is within the JPL02 uncertainty (Figure 2). The suggested increase in the rate of O+OH is consistent with Jucks *et al.* [1998], who suggested a reduction in k(O+HO₂)/k(O+OH). Two recent laboratory studies of the O+OH rate constant that report contrasting results, published as our work was being completed, are discussed in the auxiliary material¹.

3. Results and Discussion

The MLS OH profiles (Figure 1a) all peak near 45 km. Differences in peak values are due to seasonal changes in solar declination. The MLS OH observations and Mdl_{JPL02} calculations result in $\chi^2_r=12.3$, between 25-60 km and considering all seasons (see auxiliary material¹ for description of χ^2_r ; a value of 1 indicates that model profiles generally lie within measurement uncertainty). Mdl_{JPL02} overestimates observed OH between 40-60 km, often outside of the measurement uncertainty. Better agreement between modeled and measured OH is achieved for Mdl_{SmSt}. This comparison results in a $\chi^2_r=3.1$ for OH. Results for Mdl_C, described below, lead to a $\chi^2_r=1.6$ (Figure 3). The good agreement between measured OH profiles and the Mdl_C simulation at all altitudes and seasons indicates that MLS observations do not exhibit a “HO_x dilemma” as reported by Conway *et al.* [2000] for MAHRSI observations of OH.

The closest FIRS-2 observations in time (LST=13.6 hr) to the MLS overpass are shown in Figure 1a. The χ^2_r between FIRS-2 observations of OH and the three

model cases are larger than for the MLS comparison. The χ^2_r values for FIRS-2 are 16.7 for Mdl_{JPL02}, 11.8 for Mdl_{SmSt}, and 10.7 for Mdl_C (Figure 4; profiles at seven times have been used to calculate χ^2_r , as described above). These larger values are due to the influence of the higher altitude measurements of OH, which are much smaller than model values. The sense of the discrepancies between FIRS-2 OH and the Mdl_C calculation for September 2004 at various altitudes is the same as noted by *Conway et al.* [2000]. However, the FIRS-2 discrepancies are smaller, particularly near 40 km. The Mdl_C simulation provides a reasonably good description of the shape and abundance of the FIRS-2 OH profile. Hence, the FIRS-2 observations are also not consistent with a HO_x dilemma.

Figure 1b shows comparisons of measured and modeled HO₂. Mdl_{JPL02} overestimates MLS HO₂ at most altitudes, resulting in a $\chi^2_r=22.2$. In contrast to the comparison for OH, Mdl_{SmSt} results in a slightly higher value of χ^2_r (23.0) than Mdl_{JPL02}. Best agreement with MLS HO₂ is achieved by Mdl_C, with $\chi^2_r=18$. The HO₂ profile measured by FIRS-2 is generally higher than observed by MLS (Figure 1b). All three models give excellent agreement with FIRS-2 HO₂ (Figure 4).

We have determined, through a series of sensitivity studies, that a reasonably good overall description of measured OH, HO₂, HO_x, and HO₂/OH is achieved using Mdl_C, which includes a 20% increase in (1) and the SmSt94 rate for O+OH. Profiles of total HO_x and HO_x partitioning from MLS and FIRS-2 are shown in Figures 1c and 1d. The MLS profiles are affected by the oscillations in HO₂. Best agreement between measured and modeled MLS HO_x is found for Mdl_C, with a $\chi^2_r=2.9$ (Figure 3). For HO_x partitioning (e.g., HO₂/OH) measured by MLS, the two simulations using the SmSt94 rate for O+OH result in slightly poorer agreement compared to Mdl_{JPL02} (Figure 3). Conversely, for HO_x partitioning measured by FIRS-2, the two simulations using the SmSt94 rate result in better agreement compared to Mdl_{JPL02} (Figure 4). The partitioning of HO_x is sensitive to uncertainties in more model parameters than the other quantities examined here. Considering the suite of model and measured OH, HO₂, HO_x, and HO_x partitioning, represented by “Total” in Figures 3 and 4, Mdl_C kinetics leads to the best overall simulations for both the MLS ($\chi^2_r=7.8$) and FIRS-2 ($\chi^2_r=7.5$) data sets, for the suite of model simulations considered here.

If we use the JPL02 rate for O+OH, no simple change to the rate of HO₂+OH improves the simulation of both MLS OH and HO_x in a manner comparable to Mdl_C kinetics. Likewise, it is difficult to reconcile the observations and model results considering only uncertainty in the O+OH rate. The range of model calculations based on the JPL02 uncertainty in O+OH is given in the auxiliary material¹.

4. Ozone Deficit Problem

Calculated (O_x) production (P) and loss (L) rates during Fall 2004, for the three model runs, are shown in Figure 5. Production is the same for all cases because model O₃ has been constrained to the daytime MLS profile. Calculated L exceeds P throughout the upper stratosphere and lower mesosphere, consistent with an ozone deficit problem.

Introduction of the SmSt94 rate for O+OH leads to an increase in calculated HO₂ compared to Mdl_{JPL02}.

This increased HO₂ results in larger L-P compared to Mdl_{JPL02} because O+HO₂ is a rate determining step of O_x loss. The Mdl_C simulation results in a value of L-P that is intermediate between the other two simulations above 50 km: the increase in HO₂+OH results in lower HO_x and hence slower O_x loss by all HO_x cycles compared to the Mdl_{SmSt} simulation. A 50% reduction in the rate of O+HO₂ results in balance of P and L near 40 km, as suggested by *Summers et al.* [1997], but leads to poorer agreement with MLS and FIRS-2 HO_x profiles compared to the other simulations shown above (see auxiliary material¹).

There have been many suggestions in the literature regarding possible resolutions to the HO_x dilemma and the O₃ deficit problem. It has been suggested that reactions involving vibrationally excited O₂($\nu \geq 26$)+O₂ could solve the ozone deficit problem by providing an autocatalytic source of O_x [Miller *et al.*, 1994]. However, *Slanger and Copeland* [2003] question the existence of this reactive pathway. *Varandas* [2004] suggested reactions involving vibrationally excited O₂ and OH could be important for both the HO_x dilemma and the O₃ deficit problem. However, *Smith and Copeland* [2005] have raised doubts regarding the suggestion of *Varandas* [2004]. Our observations and simulations, taken at face value, suggest a continued need to resolve the ozone deficit problem without recourse to major perturbations in the kinetic parameters that regulate HO_x.

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¹Auxiliary material is available via Web browser or via Anonymous FTP from <ftp://ftp.agu.org/apend/>

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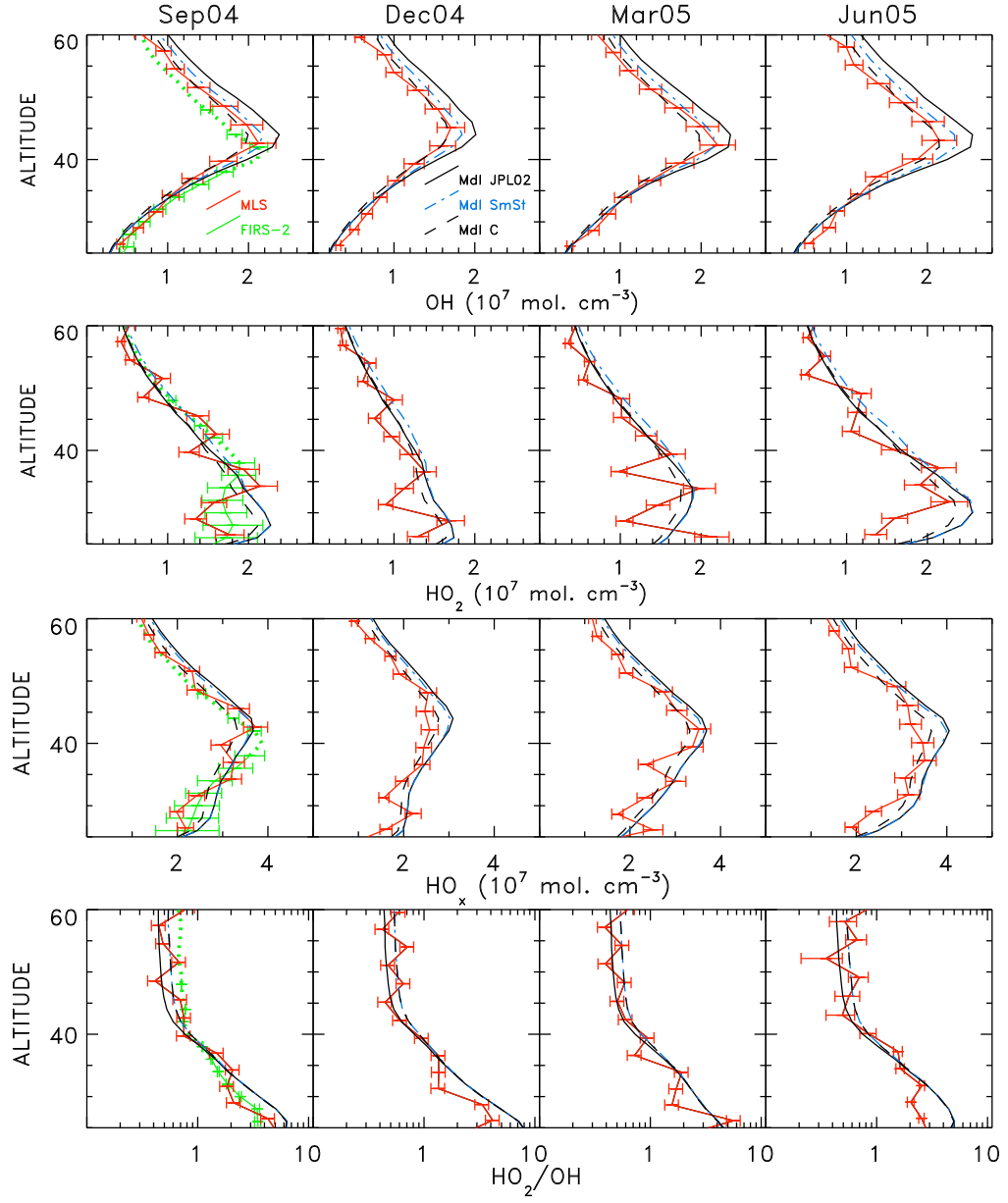


Figure 1. 1st Row: MLS OH profiles (red curve) for four seasons and model results for a) JPL02 kinetics, “Mdl_{JPL02}” (black solid), b) *Smith and Stewart* [1994] rate for O+OH, “Mdl_{SmSt}” (blue dashed dot), c) *Smith and Stewart* [1994] rate for O+OH and a 20% increase to OH+HO₂, “Mdl_C” (see text) (black dashed), FIRS-2 observations from Sept 23, 2004 (green curve, data fit to assumed profile shape above float altitude indicated by green dotted curve) are also shown. 2nd Row: same as top row except for HO₂; 3rd Row: same as top row except for HO_x, 4th Row: same as top row except for HO₂/OH.

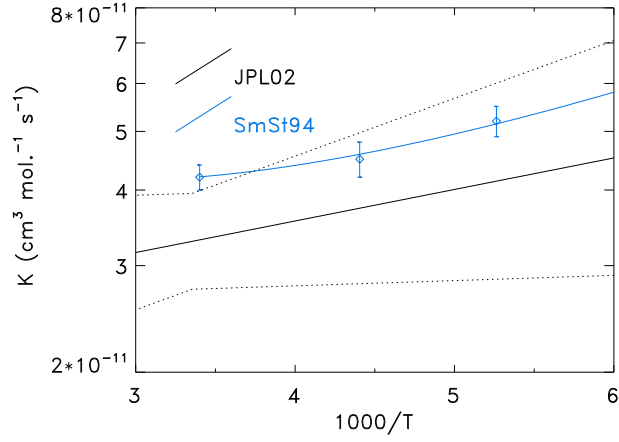


Figure 2. O+OH reaction rate from JPL02 (black) and from *Smith and Stewart* [1994] (blue). Black dotted curves denote uncertainties from JPL02.

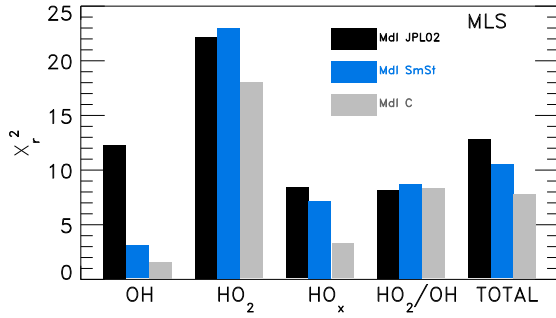


Figure 3. χ^2_r between MLS measurements and: “Mdl_{JPL02}” (black), “Mdl_{SmSt}” model (blue solid), “Mdl_C” (see text) (gray), for OH, HO₂, HO_x, and HO₂/OH. Total represents average of χ^2_r for other 4 parameters.

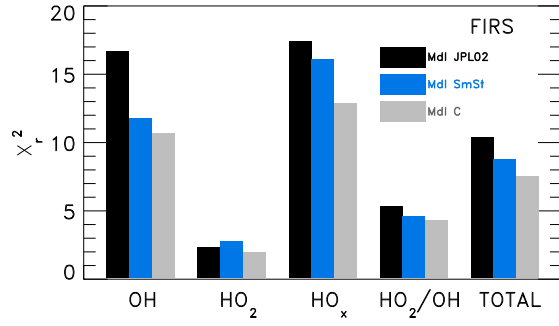


Figure 4. Same as Figure 3, except for comparison of models with FIRS-2 observations

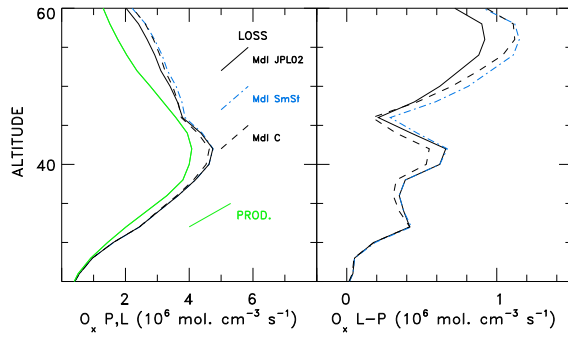


Figure 5. Left Panel: Fall 2004 production (green curve) and loss of odd oxygen from Mdl_{JPL02} (black curve), Mdl_{SmSt} (blue dashed dot), and Mdl_C (black dashed), Right panel: Loss-Production of O_x for the 3 scenarios shown in the left panel.